(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 2 231 637 B1

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
19.12.2012 Bulletin 2012/51

(21) Application number: **09701980.6**

(22) Date of filing: **14.01.2009**

(51) Int Cl.:
C07D 401/04 *(2006.01)* ***A01N 43/58*** *(2006.01)*
A61P 35/00 *(2006.01)*

(86) International application number:
PCT/EP2009/000166

(87) International publication number:
WO 2009/090039 (23.07.2009 Gazette 2009/30)

(54) **PYRIDAZINE FUNGICIDES**

PYRIDAZINFUNGIZIDE

FUNGICIDES À BASE DE PYRIDAZINE

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO SE SI SK TR

(30) Priority: **16.01.2008 GB 0800762**

(43) Date of publication of application:
29.09.2010 Bulletin 2010/39

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WO-A-2008/009406

EP 2 231 637 B1

Printed by Jouve, 75001 PARIS (FR)

Description

[0001] The present invention relates to novel pyridazine derivatives as active ingredients which have microbiocidal activity, in particular fungicidal activity. The invention also relates to preparation of these active ingredients, to novel heterocyclic derivatives used as intermediates in the preparation of these active ingredients, to preparation of these novel intermediates, to agrochemical compositions which comprise at least one of the novel active ingredients, to preparation of these compositions and to use of the active ingredients or compositions in agriculture or horticulture for controlling or preventing infestation of plants, harvested food crops, seeds or non-living materials by phytopathogenic microorganisms, preferably fungi.

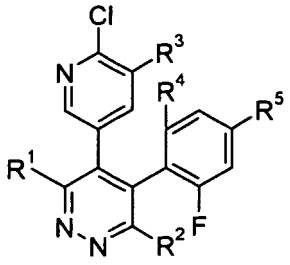
[0002] In addition, the present invention also relates to the use of these novel pyridazine derivatives as plant growth regulators (PGRs).

[0003] Furthermore, the present invention also relates to compositions comprising the novel pyridazine derivatives that improve plants, a process which is commonly and hereinafter referred to as "plant health".

[0004] The present invention further relates to the use of these novel pyridazine derivatives in the treatment of cancer and to fungicidal or pharmaceutical compositions comprising at least one of these compounds as active component.

[0005] Pyridazine derivatives as active ingredients which have microbiocidal activity, in particular fungicidal activity are known from WO08009406, EP1767529 and EP1775290

[0006] The present invention provides a compound of formula I:

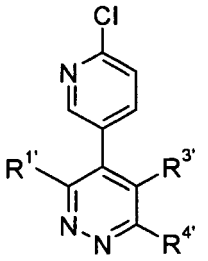


(I)

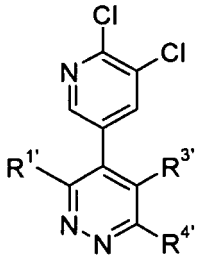
wherein

R^1 is methyl, ethyl or isopropyl;
R^2 is chloro, fluoro, hydroxy or C_1-C_2alkoxy;
R^3 is H, chloro, fluoro, methoxy or C_1-C_3alkyl;
R^4 is chloro, fluoro or bromo; and
R^5 is H, fluoro or methoxy;

or an agrochemically usable salt form thereof;
with the proviso that when R^1 is methyl, R^2 is chloro and R^3 is H, then R^4 or R^5 is different from fluoro and the compound of formula I is not (I.ae) or (I.ai) .



(I.ae)



(I.ai)

wherein $R^{1'}$, $R^{3'}$ and $R^{4'}$ are as defined as follows

$R^{1'}$	$R^{3'}$	$R^{4'}$
CH_3	2,6-difluorophenyl	Cl
CH_3	2-chloro-6-fluorophenyl	Cl

(continued)

$R^{1'}$	$R^{3'}$	$R^{4'}$
CH_3	2,6-difluoro-4-methoxyphenyl	OH
CH_3	2,6-difluoro-4-methoxyphenyl	F
CH_3	2,6-difluoro-4-methoxyphenyl	Cl
CH_3	2,6-difluoro-4-methoxyphenyl	OCH_3
CH_2CH_3	2,4-difluorophenyl	OH
CH_2CH_3	2,4-difluorophenyl	Cl
CH_2CH_3	2,4,6-trifluorophenyl	OH
CH_2CH_3	2,4,6-trifluorophenyl	Cl
CH_2CH_3	2,6-difluoro-4-methoxyphenyl	OH
CH_2CH_3	2,6-difluoro-4-methoxyphenyl	Cl

is excluded from the scope of protection.

[0007] Halogen means fluorine, chlorine, bromine or iodine.

[0008] The above or below mentioned alkyl radicals may be straight-chained or branched.

[0009] Alkyl on its own or as part of another substituent is, depending upon the number of carbon atoms mentioned, for example, methyl, ethyl, propyl, butyl, pentyl, hexyl and the isomers thereof, for example, isopropyl, isobutyl, sec-butyl, tert-butyl, isopentyl or tert-pentyl.

[0010] A haloalkyl group may contain one or more identical or different halogen atoms and, for example, may stand for CH_2Cl, $CHCl_2$, CCl_3, CH_2F, CHF_2, CF_3, CF_3CH_2, CH_3CF_2, CF_3CF_2 or CCl_3CCl_2.

[0011] Cycloalkyl on its own or as part of another substituent is, depending upon the number of carbon atoms mentioned, for example, cyclopropyl, cyclobutyl, cyclopentyl or cyclohexyl.

[0012] Alkenyl on its own or as part of another substituent is, depending upon the number of carbon atoms mentioned, for example, ethenyl, allyl, 1-propenyl, buten-2-yl, buten-3-yl, penten-1-yl, penten-3-yl, hexen-1-yl or 4-methyl-3-pentenyl.

[0013] Alkynyl on its own or as part of another substituent is, depending upon the number of carbon atoms mentioned, for example, ethynyl, propyn-1-yl, propyn-2-yl, butyn-1-yl, butyn-2-yl, 1-methyl-2-butynyl, hexyn-1-yl or 1-ethyl-2-butynyl.

[0014] The presence of one or more possible asymmetric carbon atoms in a compound of formula I means that the compounds may occur in optically isomeric, that means enantiomeric or diastereomeric forms. As a result of the presence of a possible aliphatic C=C double bond, geometric isomerism, that means cis-trans or (*E*)-(*Z*) isomerism may also occur. Also atropisomers may occur as a result of restricted rotation about a single bond. Formula I is intended to include all those possible isomeric forms and mixtures thereof. The present invention intends to include all those possible isomeric forms and mixtures thereof for a compound of formula I.

[0015] In each case, the compounds of formula I according to the invention are in free form or in an agronomically usable salt form.

[0016] Preferred subgroups of compounds of formula I according to the invention are those wherein

R^1 is methyl or ethyl;
R^2 is chloro, fluoro or methoxy;
R^3 is H, chloro or fluoro;
R^4 is chloro or fluoro; and
R^5 is H or methoxy.

[0017] Preferred individual compounds are:

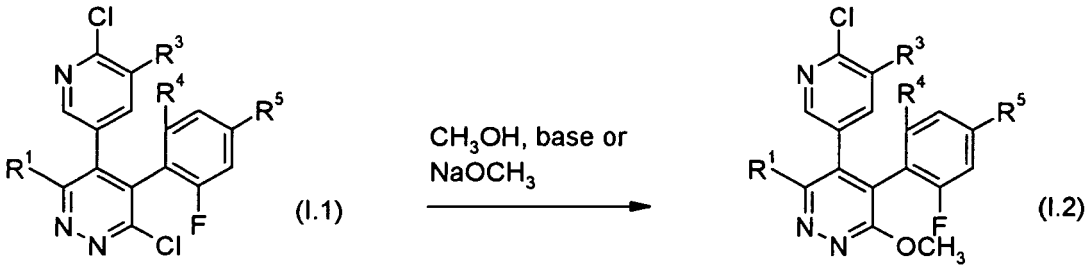
4-(6-chloro-pyridin-3-yl)-6-methoxy-3-methyl-5-(2,4,6-trifluoro-phenyl)-pyridazine;
3-chloro-5-(6-chloro-pyridin-3-yl)-6-ethyl-4-(2,4,6-trifluoro-phenyl)-pyridazine;
3-chloro-5-(5,6-dichloro-pyridin-3-yl)-6-methyl-4-(2,4,6-trifluoro-phenyl)-pyridazine;
3-chloro-5-(6-chloro-pyridin-3-yl)-6-isopropyl-4-(2,4,6-trifluoro-phenyl)-pyridazine; and

[0018] Especially preferred individual compounds are:

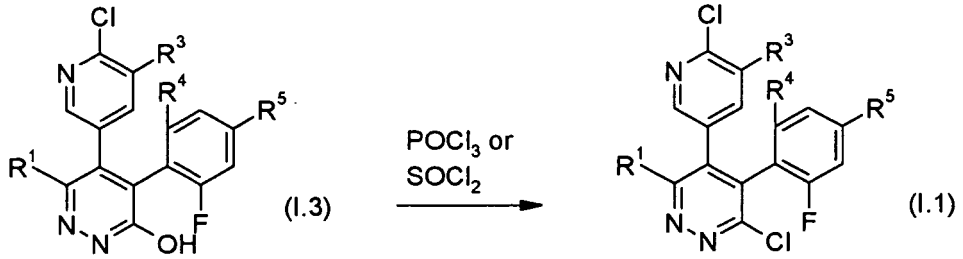
4-(6-chloro-pyridin-3-yl)-6-methoxy-3-methyl-5-(2,4,6-trifluoro-phenyl)-pyridazine;
and 3-chloro-5-(5,6-dichloro-pyridin-3-yl)-6-methyl-4-(2,4,6-trifluoro-phenyl)-pyridazine.

[0019] Certain pyridazine derivatives with aryl or heteroaryl groups in positions 4 and 5 have been proposed for controlling plant-destructive fungi, for example in WO 2005/121104, WO 2006/001175, WO 2007/066601 and WO 2007/080720. However, the action of those preparations is not satisfactory in all aspects of agricultural needs. Surprisingly, with the compounds of formula I, new kinds of fungicides having a high level of biological actitivity have now been found.

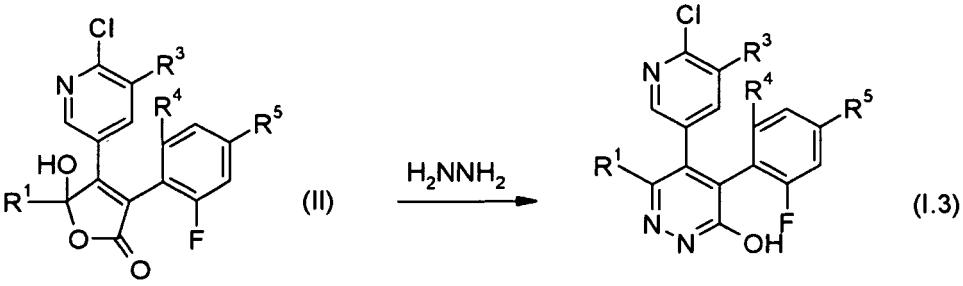
[0020] The compounds of formula I.2, wherein R^1, R^3, R^4 and R^5 are as defined for formula I, can be obtained by transformation of a compound of formula I.1, wherein R^1, R^3, R^4 and R^5 are as defined for formula I, with methanol and base or with sodium methoxide.



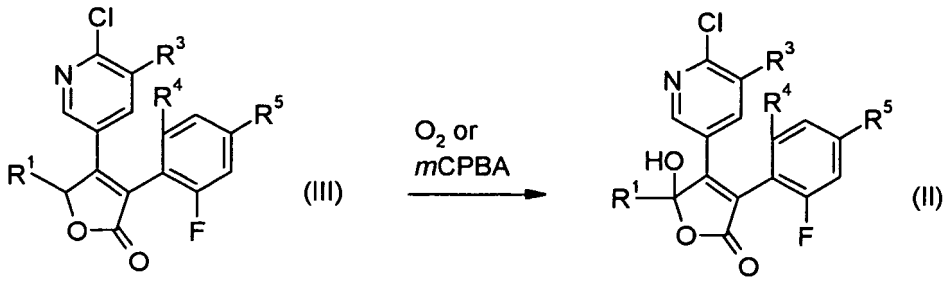
[0021] The compounds of formula 1.1, wherein R^1, R^3, R^4 and R^5 are as defined for formula I, can be obtained by transformation of a compound of formula 1.3, wherein R^1, R^3, R^4 and R^5 are as defined for formula I, with phosphorus oxychloride or thionyl chloride.



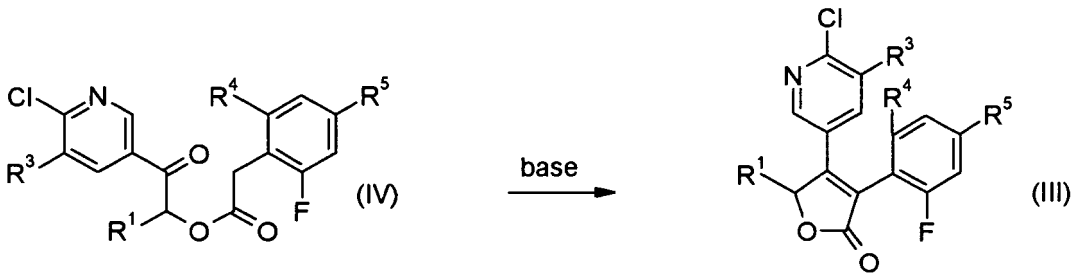
[0022] The compounds of formula 1.3, wherein R^1, R^3, R^4 and R^5 are as defined for formula I, can be obtained by transformation of a compound of formula II, wherein R^1, R^3, R^4 and R^5 are as defined for formula I, with a hydrazine derivative, e.g. hydrazine hydrate.



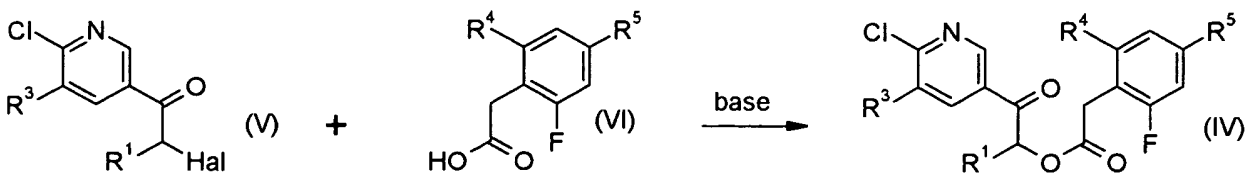
[0023] The compounds of formula II, wherein R^1, R^3, R^4 and R^5 are as defined for formula I, can be obtained by transformation of a compound of formula III, wherein R^1, R^3, R^4 and R^5 are as defined for formula I, by oxidation with oxygen, air or 3-chloroperbenzoic acid.



[0024] The compounds of formula III, wherein R^1, R^3, R^4 and R^5 are as defined for formula I, can be obtained by transformation of a compound of formula IV, wherein R^1, R^3, R^4 and R^5 are as defined for formula I, with a base, e.g. pyridine, triethylamine, diisopropylethylamine, 1,5-diazabicyclo[4.3.0]non-5-ene or 1,8-diazabicyclo[5.4.0]undec-7-ene.



[0025] The compounds of formula IV, wherein R^1, R^3, R^4 and R^5 are as defined for formula I, can be obtained by transformation of a compound of formula V, wherein R^1 and R^3 are as defined for formula I and Hal is halogen, preferably chlorine or bromine, with a compound of formula VI, wherein R^4 and R^5 is as defined for formula I, and a base, e.g. pyridine, triethylamine, diisopropylethylamine, 1,5-diazabicyclo[4.3.0]non-5-ene or 1,8-diazabicyclo[5.4.0]undec-7-ene.



[0026] Surprisingly, it has now been found that the novel compounds of formula I have, for practical purposes, a very advantageous level of biological activity for protecting plants against diseases that are caused by fungi as well as by bacteria and viruses.

[0027] The compounds of formula I can be used in unmodified form or, preferably, together with carriers and adjuvants conventionally employed in the art of formulation.

[0028] Therefore the invention also relates to compositions for controlling and protecting against phytopathogenic micro-organisms, comprising a compound of formula I and an inert carrier, and to a method of controlling or preventing infestation of useful plants by phytopathogenic micro-organisms, wherein a composition, comprising a compound of formula I as active ingredient and an inert carrier, is applied to the plants, to parts thereof or the locus thereof.

[0029] In addition, the invention could be used to protect non-living materials from fungal attack, e.g. lumber, wall boards and paint.

[0030] To this end compounds of formula I and inert carriers are conveniently formulated in known manner to mollifiable concentrates, coat able pastes, directly spray able or dilatable solutions, dilute emulsions, wet table powders, soluble powders, dusts, granulates, and also encapsulations e.g. in polymeric substances. As with the type of the compositions, the methods of application, such as spraying, atomising, dusting, scattering, coating or pouring, are chosen in accordance with the intended objectives and the prevailing circumstances. The compositions may also contain further adjuvants such as stabilizers, antifoams, viscosity regulators, binders or pacifiers as well as fertilizers, micronutrient donors or other formulations for obtaining special effects.

[0031] Suitable carriers and adjuvants can be solid or liquid and are substances useful in formulation technology, e.g. natural or regenerated mineral substances, solvents, dispersants, wetting agents, tackifiers, thickeners, binders or fertilizers. Such carriers are for example described in WO 97/33890.

[0032] The compounds of formula I or compositions, comprising a compound of formula I as active ingredient and an

inert carrier, can be applied to the locus of the plant or plant to be treated, simultaneously or in succession with further compounds. These further compounds can be e.g. fertilizers or micronutrient donors or other preparations which influence the growth of plants. They can also be selective herbicides, plant growth regulators as well as insecticides, fungicides, bactericides, nematicides, molluscicides or mixtures of several of these preparations, if desired together with further carriers, surfactants or application promoting adjuvants customarily employed in the art of formulation.

[0033] A preferred method of applying a compound of formula I, or a composition, comprising a compound of formula I as active ingredient and an inert carrier, is foliar application. The frequency of application and the rate of application will depend on the risk of infestation by the corresponding pathogen. However, the compounds of formula I can also penetrate the plant through the roots via the soil (systemic action) by drenching the locus of the plant with a liquid formulation, or by applying the compounds in solid form to the soil, e.g. in granular form (soil application). In crops of water rice such granulates can be applied to the flooded rice field. The compounds of formula I may also be applied to seeds (coating) by impregnating the seeds or tubers either with a liquid formulation of the fungicide or coating them with a solid formulation.

[0034] A formulation, i.e. a composition comprising the compound of formula I and, if desired, a solid or liquid adjuvant, is prepared in a known manner, typically by intimately mixing and/or grinding the compound with extenders, for example solvents, solid carriers and, optionally, surface-active compounds (surfactants).

[0035] The agrochemical formulations will usually contain from 0.1 to 99% by weight, preferably from 0.1 to 95% by weight, of the compound of formula I, 99.9 to 1% by weight, preferably 99.8 to 5% by weight, of a solid or liquid adjuvant, and from 0 to 25% by weight, preferably from 0.1 to 25% by weight, of a surfactant.

[0036] Whereas it is preferred to formulate commercial products as concentrates, the end user will normally use dilute formulations.

[0037] Advantageous rates of application are normally from 5g to 2kg of active ingredient (a.i.) per hectare (ha), preferably from 10g to 1kg a.i./ha, most preferably from 20g to 600g a.i./ha. When used as seed drenching agent, convenient rates of application are from 10mg to 1 g of active substance per kg of seeds. The rate of application for the desired action can be determined by experiments. It depends for example on the type of action, the developmental stage of the useful plant, and on the application (location, timing, application method) and can, owing to these parameters, vary within wide limits.

[0038] The invention relates to a method of controlling or preventing infestation of useful plants by phytopathogenic micro-organisms, wherein a compound of formula I is applied as active ingredient to the plants, to parts thereof or the locus thereof. The compounds of formula I according to the invention are distinguished by excellent activity at low rates of application, by being well tolerated by plants and by being environmentally safe. They have very useful curative, preventive and systemic properties and are used for protecting numerous useful plants. The compounds of formula I can be used to inhibit or destroy the diseases that occur on plants or parts of plants (fruit, blossoms, leaves, stems, tubers, roots) of different crops of useful plants, while at the same time protecting also those parts of the plants that grow later e.g. from phytopathogenic micro-organisms.

[0039] It is also possible to use compounds of formula I as dressing agents for the treatment of plant propagation material, in particular of seeds (fruit, tubers, grains) and plant cuttings (e.g. rice), for the protection against fungal infections as well as against phytopathogenic fungi occurring in the soil.

[0040] Furthermore the compounds of formula I according to the invention may be used for controlling fungi in related areas, for example in the protection of technical materials, including wood and wood related technical products, in food storage or in hygiene management.

[0041] Within the scope of the invention, useful plants to be protected typically comprise the following groups of plants: cereals (wheat, barley, rye, oat, rice, maize, sorghum and related species); beets (sugar beet and fodder beet); pomes, drupes and soft fruit (apples, pears, plums, peaches, almonds, cherries, strawberries, raspberries and blackberries); leguminous plants (beans, lentils, peas, soybeans); oil plants (rape, mustard, poppy, olives, sunflowers, coconut, castor oil plants, cocoa beans, groundnuts); cucurbit plants (pumpkins, cucumbers, melons); fibre plants (cotton, flax, hemp, jute); citrus fruit (oranges, lemons, grapefruit, mandarins); vegetables (spinach, lettuce, asparagus, cabbages, carrots, onions, tomatoes, potatoes, paprika); lauraceae (avocado, cinnamomum, camphor) or plants such as tobacco, nuts, coffee, eggplants, sugar cane, tea, pepper, vines, hops, bananas and natural rubber plants, as well as ornamentals.

[0042] The term "useful plants" and / or "target crops" is to be understood as including also useful plants that have been rendered tolerant to herbicides like bromoxynil or classes of herbicides (such as, for example, HPPD inhibitors, ALS inhibitors, for example primisulfuron, prosulfuron and trifloxysulfuron, EPSPS (5-enol-pyrovyl-shikimate-3-phosphate-synthase) inhibitors, GS (glutamine synthetase) inhibitors or PPO (protoporphyrinogen-oxidase) inhibitors) as a result of conventional methods of breeding or genetic engineering. An example of a crop that has been rendered tolerant to imidazolinones, e.g. imazamox, by conventional methods of breeding (mutagenesis) is Clearfield® summer rape (Canola). Examples of crops that have been rendered tolerant to herbicides or classes of herbicides by genetic engineering methods include glyphosate- and glufosinate-resistant maize varieties commercially available under the trade names RoundupReady®, Herculex I® and LibertyLink®.

[0043] The term "useful plants" and / or "target crops" is to be understood as including also useful plants which have been so transformed by the use of recombinant DNA techniques that they are capable of synthesising one or more selectively acting toxins, such as are known, for example, from toxin-producing bacteria, especially those of the genus Bacillus.

[0044] The term "useful plants" and / or "target crops" is to be understood as including also useful plants which have been so transformed by the use of recombinant DNA techniques that they are capable of synthesising antipathogenic substances having a selective action, such as, for example, the so-called "pathogenesis-related proteins" (PRPs, see e.g. EP-A-0 392 225). Examples of such antipathogenic substances and transgenic plants capable of synthesising such antipathogenic substances are known, for example, from EP-A-0 392 225, WO 95/33818, and EP-A-0 353 191. The methods of producing such transgenic plants are generally known to the person skilled in the art and are described, for example, in the publications mentioned above.

[0045] The term "locus" of a useful plant as used herein is intended to embrace the place on which the useful plants are growing, where the plant propagation materials of the useful plants are sown or where the plant propagation materials of the useful plants will be placed into the soil. An example for such a locus is a field, on which crop plants are growing.

[0046] The term "plant propagation material" is understood to denote generative parts of the plant, such as seeds, which can be used for the multiplication of the latter, and vegetative material, such as cuttings or tubers, for example potatoes. There may be mentioned for example seeds (in the strict sense), roots, fruits, tubers, bulbs, rhizomes and parts of plants. Germinated plants and young plants which are to be transplanted after germination or after emergence from the soil, may also be mentioned. These young plants may be protected before transplantation by a total or partial treatment by immersion. Preferably "plant propagation material" is understood to denote seeds.

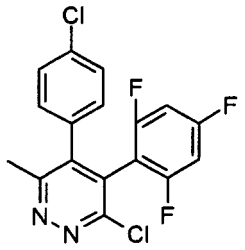
[0047] The compounds of formula I are, for example, effective against the phytopathogenic fungi of the following classes: The compounds of formula I are, for example, effective against the phytopathogenic fungi of the following classes: Fungi imperfecti (e.g. *Alternaria* spp.), Basidiomycetes (e.g. *Corticium* spp., *Ceratobasidium* spp., *Waitea* spp., *Thanatephorus* spp., *Rhizoctonia* spp., *Hemileia* spp., *Puccinia* spp., *Phakopsora* spp., *Ustilago* spp., *Tilletia* spp.), Ascomycetes (e.g. *Venturia* spp., *Blumeria* spp., *Erysiphe* spp., *Podosphaera* spp., *Uncinula* spp., *Monilinia* spp., *Sclerotinia* spp., *Colletotrichum* spp., *Glomerella* spp., *Fusarium* spp., *Gibberella* spp., *Monographella* spp., *Phaeosphaeria* spp., *Mycosphaerella* spp., *Cercospora* spp., *Pyrenophora* spp., *Rhynchosporium* spp., *Magnaporthe* spp., *Gaeumannomyces* spp., *Oculimacula* spp., *Ramularia* spp., *Botryotinia* spp.) and Oomycetes (e.g. *Phytophthora* spp., *Pythium* spp., *Plasmopara* spp., *Peronospora* spp., *Pseudoperonospora* spp. *Bremia* spp). Outstanding activity has been observed against powdery mildews (e.g. *Uncinula necator,* rusts (e.g. *Puccinia* spp.) and leaf spots (e.g. *Mycosphaerella* spp.). Furthermore, the novel compounds of formula I are effective against phytopathogenic gram negative and gram positive bacteria (e.g. *Xanthomonas* spp, *Pseudomonas* spp, *Erwinia amylovora, Ralstonia* spp.) and viruses (e.g. tobacco mosaic virus).

[0048] The compounds of formula I are normally used in the form of fungicidal compositions for controlling or protecting against phytopathogenic microorganisms, comprising as active ingredient at least one compound of formula I or at least one preferred individual compound as above-defined, in free form or in agrochemically usable salt form, and at least one of the above-mentioned adjuvants.

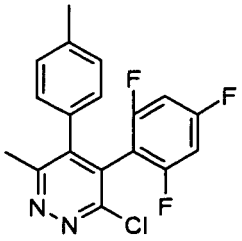
[0049] Said fungicidal compositions for controlling or protecting against phytopathogenic microorganisms, comprising as active ingredient at least one compound of formula I or at least one preferred individual compound as above-defined, in free form or in agrochemically usable salt form, and at least one of the above-mentioned adjuvants can be mixed with other fungicides, resulting in some cases in unexpected synergistic activities. Mixing components which are particularly preferred are:

Azoles, such as azaconazole, BAY 14120, bitertanol, bromuconazole, cyproconazole, difenoconazole, diniconazole, epoxiconazole, fenbuconazole, fluquinconazole, flusilazole, flutriafol, hexaconazole, imazalil, imibenconazole, ipconazole, metconazole, myclobutanil, pefurazoate, penconazole, prothioconazole, pyrifenox, prochloraz, propiconazole, simeconazole, tebuconazole, tetraconazole, triadimefon, triadimenol, triflumizole, triticonazole;
Pyrimidinyl carbinoles, such as ancymidol, fenarimol, nuarimol;
2-amino-pyrimidines, such as bupirimate, dimethirimol, ethirimol;
Morpholines, such as dodemorph, fenpropidine, fenpropimorph, spiroxamine, tridemorph;
Anilinopyrimidines, such as cyprodinil, mepanipyrim, pyrimethanil;
Pyrroles, such as fenpiclonil, fludioxonil;
Phenylamides, such as benalaxyl, furalaxyl, metalaxyl, R-metalaxyl, ofurace, oxadixyl;
Benzimidazoles, such as benomyl, carbendazim, debacarb, fuberidazole, thiabendazole;
Dicarboximides, such as chlozolinate, dichlozoline, iprodione, myclozoline, procymidone, vinclozoline;
Carboxamides, such as boscalid, carboxin, fenfuram, flutolanil, mepronil, oxycarboxin, penthiopyrad, thifluzamide;
guanidines, such as guazatine, dodine, iminoctadine;
Strobilurines, such as azoxystrobin, dimoxystrobin, enestroburin, fluoxastrobin, kresoxim-methyl, metominostrobin,

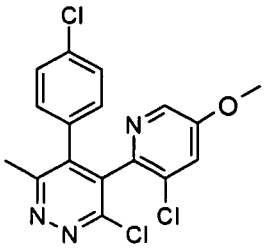
trifloxystrobin, orysastrobin, picoxystrobin, pyraclostrobin;
Dithiocarbamates, such as ferbam, mancozeb, maneb, metiram, propineb, thiram, zineb, ziram;
N-halomethylthiotetrahydrophthalimides, such as captafol, captan, dichlofluanid, fluoromides, folpet, tolyfluanid;
Cu-compounds, such as Bordeaux mixture, copper hydroxide, copper oxychloride, copper sulfate, cuprous oxide, mancopper, oxine-copper;
Nitrophenol-derivatives, such as dinocap, nitrothal-isopropyl;
Organo-phosphorus-derivatives, such as edifenphos, iprobenphos, isoprothiolane, phosdiphen, pyrazophos, tolclofos-methyl;
Pyridazine-derivatives which are known and may be prepared by methods as described in WO 05/121104, WO 06/001175 and WO 07/066601, such as 3-chloro-5-(4-chloro-phenyl)-6-methyl-4-(2,4,6-trifluoro-phenyl)-pyridazine (formula P.1), 3-chloro-6-methyl-5-p-tolyl-4-(2,4,6-trifluoro-phenyl)-pyridazine (formula P.2) and 3-chloro-4-(3-chloro-5-methoxy-pyridin-2-yl)-5-(4-chloro-phenyl)-6-methyl-pyridazine (formula P.3);



P.1

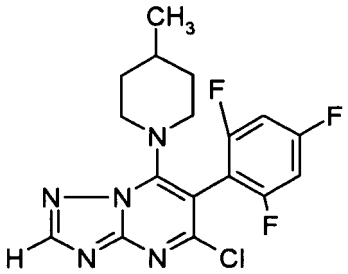


P.2



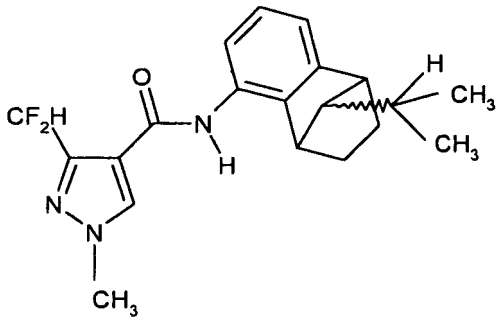
P.3

Triazolopyrimidine derivatives which are known and may be prepared by methods as described in WO98/46607, such as 5-chloro-7-(4-methyl-piperidin-1-yl)-6-(2,4,6-trifluorophenyl)- [1,2,4]triazolo[1,5-a]pyrimidine (formula T.1);

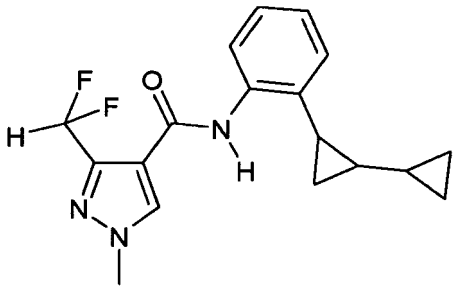


T.1

Carboxamide derivatives which are known and may be prepared by methods as described in WO04/035589, WO06/37632, WO03/074491 or WO03070705, such as 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid (9-isopropyp-1,2,3,4-tetrahaydro-1,4-methano-naphthalen-5-yl)-amide (formula U.1), 3-difluoromethyl-1-methyl-1 H-pyrazole-4-carboxylic acid (2-bicyclopropyl-2-yl-phenyl)-amide (formula U.2) or N-(3',4'-dichloro-5-fluoro-1,1'-biphenyl-2-yl)-3-(difluoromethyl)-1-methyl-1H-pyrazole-4-carboxamide;

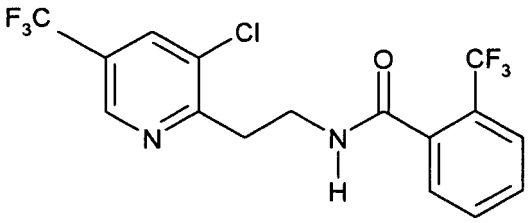


U.1;



U.2

Benzamide derivatives which are known and may be prepared by methods as described in WO 2004/016088, such as N-{-2-[3-chloro-5-(trifluoromethyl)-2-pyridinyl]ethyl}-2-trifluoromethylbenzamide, which is also known under the name fluopyram (formula V.1);



V.1

and

[0050] Various others, such as acibenzolar-S-methyl, anilazine, benthiavalicarb, blasticidin-S, chinomethionate, chloroneb, chlorothalonil, cyflufenamid, cymoxanil, dichlone, diclocymet, diclomezine, dicloran, diethofencarb, dimethomorph, flumorph, dithianon, ethaboxam, etridiazole, famoxadone, fenamidone, fenoxanil, fentin, ferimzone, fluazinam, fluopicolide, flusulfamide, fenhexamid, fosetyl-aluminium, hymexazol, iprovalicarb, cyazofamid, kasugamycin, mandipropamid, methasulfocarb, metrafenone, nicobifen, pencycuron, phthalide, polyoxins, probenazole, propamocarb, proquinazid, pyroquilon, quinoxyfen, quintozene, sulfur, tiadinil, triazoxide, tricyclazole, triforine, validamycin, zoxamide and glyphosate.

[0051] Another aspect of invention is related to the use of a compound of formula I or of a preferred individual compound as above-defined, of a composition comprising at least one compound of formula I or at least one preferred individual compound as above-defined, or of a fungicidal mixture comprising at least one compound of formula I or at least one preferred individual compound as above-defined, in admixture with other fungicides, as described above, for controlling or preventing infestation of plants, harvested food crops, seeds or non-living materials by phytopathogenic microorganisms, preferably fungal organisms.

[0052] A further aspect of invention is related to a method of controlling or preventing an infestation of crop plants, harvested food crops or of non-living materials by phytopathogenic or spoilage microorganisms or organisms potentially harmful to man, especially fungal organisms, which comprises the application of a compound of formula I or of a preferred individual compound as above-defined as active ingredient to the plants, to parts of the plants or to the locus thereof, to seeds or to any part of the non-living materials.

[0053] Controlling or preventing means reducing the infestation of crop plants or of non-living materials by phytopathogenic or spoilage microorganisms or organisms potentially harmful to man, especially fungal organisms, to such a level that an improvement is demonstrated.

[0054] Surprisingly, the pyridazine compounds of formula I according to the invention, in particular the individual pyridazine compounds described in the above description as being preferred, also present a plant growth regulator (PGR) activity. Therefore, the present invention also relates to the use of these novel pyridazine derivatives as plant growth regulators (PGRs).

[0055] Plant growth regulators (PGRs) are generally any substances or mixtures of substances intended to accelerate or retard the rate of growth or maturation, or otherwise alter the development of plants or their produce.

[0056] Plant growth regulators (PGRs) affect growth and differentiation of plants.

[0057] More specifically, various plant growth regulators (PGRs) can, for example, reduce plant height, stimulate seed germination, induce flowering, darken leaf coloring, change the rate of plant growth and modify the timing and efficiency of fruiting.

[0058] Furthermore, the present invention also relates to compositions comprising the novel pyridazine derivatives of the present invention that improve plants, a process which is commonly and hereinafter referred to as "plant health".

[0059] For example, advantageous properties that may be mentioned are improved crop characteristics including: emergence, crop yields, protein content, increased vigour, faster maturation, increased speed of seed emergence, improved nitrogen utilization efficiency, improved water use efficiency, improved oil content and /or quality, improved digestibility, faster ripening, improved flavor, improved starch content, more developed root system (improved root growth), improved stress tolerance (e.g. against drought, heat, salt, light, UV, water, cold), reduced ethylene (reduced production and/or inhibition of reception), tillering increase, increase in plant height, bigger leaf blade, less dead basal leaves, stronger tillers, greener leaf color, pigment content, photosynthetic activity, less input needed (such as fertilizers or water), less seeds needed, more productive tillers, earlier flowering, early grain maturity, less plant verse (lodging), increased shoot growth, enhanced plant vigor, increased plant stand and early and better germination.

[0060] Advantageous properties, obtained especially from treaded seeds, are e.g. improved germination and field establishment, better vigor, more homogeneous field establishment.

[0061] Advantageous properties, obtained especially from foliar and/or in-furrow application are e.g. improved plant growth and plant development, better growth, more tillers, greener leafes, largers leaves, more biomass, better roots, improved stress tolerance of the plants, more grain yield, more biomass harvested, improved quality of the harvest (content of fatty acids, metabolites, oil etc), more marketable products (e.g. improved size), improved process (e.g. longer shelf-life, better extraction of compounds), improved quality of seeds (for being seeded in the following seasons for seed production); or any other advantages familiar to a person skilled in the art.

[0062] It is therefore an object of the present invention to provide a method which solves the problems outlined above.

[0063] The present invention relates to plant-protecting active ingredients that are pyridazine compounds of formula I according to the invention, in particular the individual pyridazine compounds described in the above description as being preferred, and mixtures with increased efficacy and to a method of improving the health of plants by applying said compounds and mixtures to the plants or the locus thereof.

[0064] The action of the compounds of formula I goes beyond the known fungicidal action. The pyridazine compounds of formula I according to the invention, in particular the individual pyridazine compounds described in the above description as being preferred compounds exhibit plant health

[0065] The term plant health comprises various sorts of improvements of plants that are not connected to the control of harmful fungi.

[0066] The following examples illustrate the above-described invention in more detail.

[0067] However, the following compounds do not form part of the present invention: 3-chloro-4-(2-chloro-6-fluoro-phenyl)-5-(6-chloro-pyridin-3-yl)-6-methyl-pyridazine;, 3-chloro-5-(6-chloro-pyridin-3-yl)-4-(2,6-difluoro-4-methoxy-phenyl)-6-methyl-pyridazine; 4-(6-chloro-pyridin-3-yl)-5-(2,6-difluoro-4-methoxyphenyl)-6-methoxy-3-methyl-pyridazine, 3-chloro-4-(2-chloro-6-fluoro-phenyl)-5-(6-chloro-pyridin-3-yl)-6-methyl-pyridazine; 3-chloro-5-(6-chloro-pyridin-3-yl)-6-ethyl-4-(2,4,6-trifluoro-phenyl)-pyridazine;

Example 1: This example illustrates the preparation of 3-chloro-4-(2-chloro-6-fluoro-phenyl)-5-(6-chloro-pyridin-3-yl)-6-methyl-pyridazine (Compound No.I.a.02)

a) Preparation of 2-bromo-1-(6-chloro-pyridin-3-yl)-propan-1-one

[0068] Bromine (45.4 g) is slowly added to the mixture of 1-(6-chloro-pyridin-3-yl)-propan-1-one (48.2 g), 0.4 ml of hydrobromic acid (33 % solution in acetic acid) and 250 ml of acetic acid at room temperature under a nitrogen atmosphere. Subsequently, the mixture is slowly heated to 80 °C. The reaction mixture is stirred at 80 °C for 30 min, during which a yellow suspension is formed, then cooled down to 10 °C and filtered. The solid remainder is washed with tert-butyl methyl ether to deliver 2-bromo-1-(6-chloro-pyridin-3-yl)-propan-1-one hydrobromide as a yellowish solid. To a suspension of this intermediate in 800 ml of tert-butyl methyl ether is added 400 ml of a saturated aqueous sodium bicarbonate solution and the reaction mixture is stirred for 15 min. The phases are separated, the organic layer is washed with brine, dried over sodium sulfate and concentrated under reduced pressure to obtain 2-bromo-1-(6-chloro-pyridin-3-yl)-propan-1-one as an oil.

b) Preparation of 3-(2-chloro-6-fluoro-phenyl)-4-(6-chloro-pyridin-3-yl)-5-hydroxy-5-methyl-5H-furan-2-one (Compound No. II.a.1)

[0069] Triethylamine (1.0 g) is slowly added to a solution of 2-bromo-1-(6-chloro-pyridin-3-yl)-propan-1-one (2.5 g),

2-chloro-6-fluorophenylacetic acid (1.9 g) in 50 ml of acetonitrile and this mixture is stirred for 16 h at room temperature. Subsequently 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 3.4 g) is slowly added under cooling and stirring is continued for further 2 h. Then air is blown through the reaction mixture for 3 h. The reaction mixture is poured into an aqueous ammonium chloride solution and the mixture is extracted with ethyl acetate. The combined organic layer is washed with brine, dried over sodium sulfate and evaporated under reduced pressure. The remainder is purified by chromatography on silica gel, using a mixture of heptane / ethyl acetate 2 : 1 as eluent to obtain 3-(2-chloro-6-fluoro-phenyl)-4-(6-chloro-pyridin-3-yl)-5-hydroxy-5-methyl-5H-furan-2-one (Compound No. II.a.1) as white foam.

c) Preparation of 4-(2-chloro-6-fluoro-phenyl)-5-(6-chloro-pyridin-3-yl)-6-methyl-2H-pyridazin-3-one (Compound No. I.a. 01)

[0070] Hydrazine hydrate (12 g) is added to a solution of 3-(2-chloro-6-fluoro-phenyl)-4-(6-chloro-pyridin-3-yl)-5-hydroxy-5-methyl-5H-furan-2-one (Compound No. II.a.1, 80 g) in 400 ml of 1-butanol and this mixture is heated for 7 h to 120 °C. Subsequently, the mixture is poured into 400 ml of tert-butyl methyl ether. The resulting mixture is stirred for 30 min, then cooled to 0 °C and filtered. The solid remainder is washed with tert-butyl methyl ether to deliver 4-(2-chloro-6-fluoro-phenyl)-5-(6-chloro-pyridin-3-yl)-6-methyl-2H-pyridazin-3-one (Compound No. I.a.01) as colourless solid.

[0071] d) A mixture of 4-(2-chloro-6-fluoro-phenyl)-5-(6-chloro-pyridin-3-yl)-6-methyl-2H-pyridazin-3-one (Compound No. I.a.01, 57 g) and 160 ml of phosphorus oxychloride is heated at 110 °C for 1 h. After cooling the reaction mixture is evaporated under reduced pressure. The remainder is taken up with ethyl acetate and water and the phases are separated. The organic layer is washed with water and brine, dried over sodium sulfate and evaporated under reduced pressure. The residue is recrystallised from toluene to deliver 3-chloro-4-(2-chloro-6-fluoro-phenyl)-5-(6-chloro-pyridin-3-yl)-6-methyl-pyridazine (Compound No.I.a.02) as beige crystals, m.p. 166 - 167 °C.

Example 2: This example illustrates the preparation of 4-(6-chloro-pyridin-3-yl)-6-methoxy-3-methyl-5-(2,4,6-trifluoro-phenyl)-pyridazine (Compound No.I.a.12)

[0072] A mixture of 3-chloro-5-(6-chloro-pyridin-3-yl)-6-methyl-4-(2,4,6-trifluorophenyl)-pyridazine (Compound No.I.a. 11, 700 mg), sodium methoxide (30% solution in methanol, 750 mg) and 10 ml of methanol is heated for 6 h to 60 °C. Subsequently the reaction mixture is cooled, diluted with water and extracted with ethyl acetate. The combined organic layer is washed with water and brine, dried over sodium sulfate and evaporated under reduced pressure. The remainder is purified by chromatography on silica gel, using a mixture of heptane / ethyl acetate 3 : 1 as eluent to obtain 4-(6-chloro-pyridin-3-yl)-6-methoxy-3-methyl-5-(2,4,6-trifluoro-phenyl)-pyridazine (Compound I.a.12), m.p. 123-124 °C.

[0073] Tables 1 and 2 below illustrate examples of individual compounds of formula I and formula II according to the invention.

Table 1: individual compounds of formula I according to the invention

Compound No.	R^1	R^6	R^2
01	CH_3	2-chloro-6-fluoro-phenyl	OH
02	CH_3	2-chloro-6-fluoro-phenyl	Cl
03	CH_3	2-chloro-6-fluoro-phenyl	OCH_3
04	CH_2CH_3	2-chloro-6-fluoro-phenyl	OH
05	CH_2CH_3	2-chloro-6-fluoro-phenyl	Cl
06	CH_2CH_3	2-chloro-6-fluoro-phenyl	OCH_3
07	$CH(CH_3)_2$	2-chloro-6-fluoro-phenyl	OH
08	$CH(CH_3)_2$	2-chloro-6-fluoro-phenyl	Cl
09	$CH(CH_3)_2$	2-chloro-6-fluoro-phenyl	OCH_3
10	CH_3	2,4,6-trifluoro-phenyl	OH
11	CH_3	2,4,6-trifluoro-phenyl	Cl
12	CH_3	2,4,6-trifluoro-phenyl	OCH_3
13	CH_2CH_3	2,4,6-trifluoro-phenyl	OH
14	CH_2CH_3	2,4,6-trifluoro-phenyl	Cl

(continued)

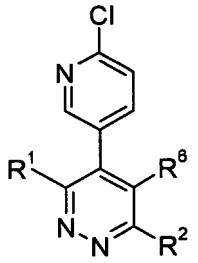
Compound No.	R^1	R^6	R^2
15	CH_2CH_3	2,4,6-trifluoro-phenyl	OCH_3
16	$CH(CH_3)_2$	2,4,6-trifluoro-phenyl	OH
17	$CH(CH_3)_2$	2,4,6-trifluoro-phenyl	Cl
18	$CH(CH_3)_2$	2,4,6-trifluoro-phenyl	OCH_3
19	CH_3	2,6-difluoro-4-methoxy-phenyl	OH
20	CH_3	2,6-difluoro-4-methoxy-phenyl	Cl
21	CH_3	2,6-difluoro-4-methoxy-phenyl	OCH_3
22	CH_2CH_3	2,6-difluoro-4-methoxy-phenyl	OH
23	CH_2CH_3	2,6-difluoro-4-methoxy-phenyl	Cl
24	CH_2CH_3	2,6-difluoro-4-methoxy-phenyl	OCH_3
25	$CH(CH_3)_2$	2,6-difluoro-4-methoxy-phenyl	OH
26	$CH(CH_3)_2$	2,6-difluoro-4-methoxy-phenyl	Cl
27	$CH(CH_3)_2$	2,6-difluoro-4-methoxy-phenyl	OCH_3

[0074] As shown above, Table 1 provides 27 specific compounds of Formula (I). Structural examples of these compounds are shown below in Formulas (I.a) through (I.g) wherein R^1, R^2 and R^6 are defined in Table 1.

[0075] However, the following compounds do not form part of the present invention:

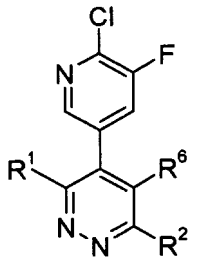
[0076] 3-chloro-4-(2-chloro-6-fluoro-phenyl)-5-(6-chloro-pyridin-3-yl)-6-methyl-pyridazine;, 3-chloro-5-(6-chloro-pyridin-3-yl)-4-(2,6-difluoro-4-methoxy-phenyl)-6-methyl-pyridazine; 4-(6-chloro-pyridin-3-yl)-5-(2,6-difluoro-4-methoxy-phenyl)-6-methoxy-3-methyl-pyridazine, 3-chloro-4-(2-chloro-6-fluoro-phenyl)-5-(6-chloro-pyridin-3-yl)-6-methyl-pyridazine; 3-chloro-5-(6-chloro-pyridin-3-yl)-6-ethyl-4-(2,4,6-trifluoro-phenyl)-pyridazine;

a) Formula (I.a):



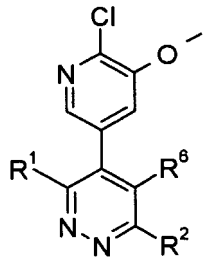
(I.a)

b) Formula (I.b):



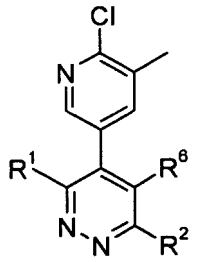
(I.b)

c) Formula (I.c):



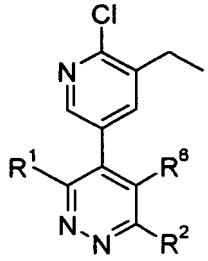
(I.c)

d) Formula (I.d):



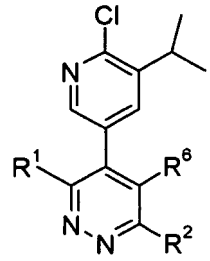
(I.d)

e) Formula (I.e):



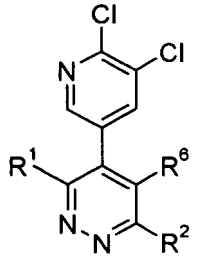
(I.e)

f) Formula (I.f):



(I.f)

g) Formula (I.g):



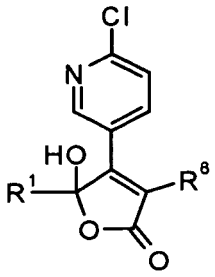
(I.g)

Table 2: individual compounds of formula II according to the invention

Compound No.	R^1	R^6
1	CH_3	2-chloro-6-fluoro-phenyl
2	CH_2CH_3	2-chloro-6-fluoro-phenyl
3	$CH(CH_3)_2$	2-chloro-6-fluoro-phenyl
4	CH_3	2,4,6-trifluoro-phenyl
5	CH_2CH_3	2,4,6-trifluoro-phenyl
6	$CH(CH_3)_2$	2,4,6-trifluoro-phenyl
7	CH_3	2,6-difluoro-4-methoxy-phenyl
8	CH_2CH_3	2,6-difluoro-4-methoxy-phenyl
9	$CH(CH_3)_2$	2,6-difluoro-4-methoxy-phenyl

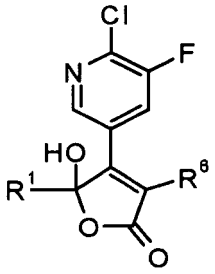
[0077] As shown above, Table 2 provides 9 specific compounds of Formula (II). Structural examples of these compounds are shown below in Formulas (II.a) through (II.g) wherein R^1 and R^6 are defined in Table 2.

a) Formula (II.a):



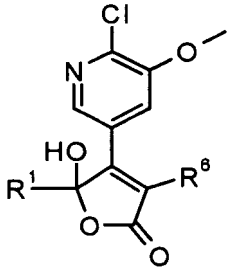
(II.a)

b) Formula (1I.b):



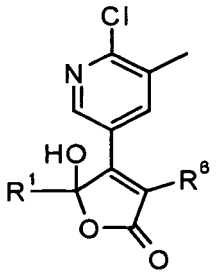
(II.b)

c) Formula (II.c):



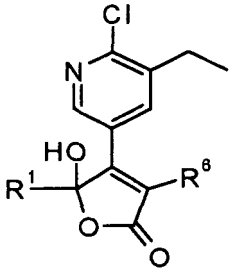
(II.c)

d) Formula (II.d):



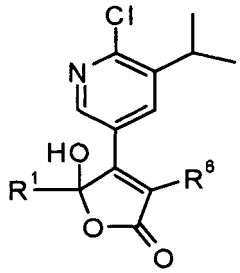
(II.d)

e) Formula (II.e):



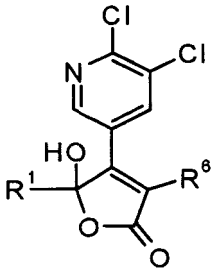
(II.e)

f) Formula (II.f):



(II.f)

g) Formula (II.g):



(II.g)

[0078] Table 3 shows selected melting point for compounds of Tables 1 and 2. Temperatures are given in degrees Celsius.

Table 3: Melting point for compounds of Tables 1 and 2

Compound Number	m.p. (°C)
I.a.02	166 - 167
I.a.12	123 - 124
I.a.14	125 - 126
I.a.20	148 - 149

(continued)

Compound Number	m.p. (°C)
I.a.17	146 - 149
I.g.11	185 - 188

[0079] The compounds according to the present invention can be prepared according to the above-mentioned reaction schemes, in which, unless otherwise stated, the definition of each variable is as defined above for a compound of formula (I).

Biological examples

[0080] *Alternaria solani* / tomato / preventive (Action against Alternaria on tomato) 4 weeks old tomato plants cv. Roter Gnom are treated with the formulated test compound in a spray chamber. Two days after application tomato plants are inoculated by spraying a spore suspension on the test plants. After an incubation period of 4 days at 22 °C / 18 °C and 95% r. h. in a greenhouse the disease incidence is assessed.
[0081] Compounds I.a.02, I.a.12, I.a.14 and I.a.20 according to the invention at 200 ppm inhibit fungal infestation in this test to at least 80 %, while under the same conditions untreated control plants are infected by the phytopathogenic fungi to over 80 %.

Botryotinia fuckeliana (Botrytis cinerea) / tomato / preventive (Action against Botrytis on tomato)

[0082] 4 weeks old tomato plants cv. Roter Gnom are treated with the formulated test compound in a spray chamber. Two days after application tomato plants are inoculated by spraying a spore suspension on the test plants. After an incubation period of 3 days at 20 °C and 95% r. h. in a greenhouse the disease incidence is assessed.
[0083] Compounds I.a.02 and I.a.12 according to the invention at 200 ppm inhibit fungal infestation in this test to at least 80 %, while under the same conditions untreated control plants are infected by the phytopathogenic fungi to over 80 %.

Puccinia recondita f. sp. *tritici* /wheat / preventive (Action against brown rust on wheat)

[0084] 1 week old wheat plants cv. Arina are treated with the formulated test compound in a spray chamber. One day after application wheat plants are inoculated by spraying a spore suspension (1 x 105 uredospores/ml) on the test plants. After an incubation period of 1 day at 20 °C and 95% r. h. plants are kept for 10 days 20 °C / 18 °C (day/night) and 60% r.h. in a greenhouse. The disease incidence is assessed 11 days after inoculation.
[0085] Compounds I.a.02, I.a.12, I.a.14 and I.a.20 according to the invention at 200 ppm inhibit fungal infestation in this test to at least 80 %, while under the same conditions untreated control plants are infected by the phytopathogenic fungi to over 80 %.
[0086] *Magnaporthe grisea (Pyricularia oryzae)* / rice / preventive (Action against rice blast) 3 weeks old rice plants cv. Koshihikari are treated with the formulated test compound in a spray chamber. Two days after application rice plants are inoculated by spraying a spore suspension (1 x 10^5 conidia/ml) on the test plants. After an incubation period of 6 days at 25°C and 95% r. h. the disease incidence is assessed.
[0087] Compounds I.a.02, I.a.14, I.a.20 and I.g.11 according to the invention at 200 ppm inhibit fungal infestation in this test to at least 80 %, while under the same conditions untreated control plants are infected by the phytopathogenic fungi to over 80 %.

Pyrenophora teres (Helminthosporium teres) / barley / preventive (Action against net blotch on barley)

[0088] 1-week-old barley plants cv. Regina are treated with the formulated test compound in a spray chamber. Two days after application barley plants are inoculated by spraying a spore suspension (2.6 x 10^4 conidia/ml) on the test plants. After an incubation period of 4 days at 20 °C and 95% r. h. the disease incidence is assessed.
[0089] Compounds I.a.02, I.a.12, I.a.14 and I.a.20 according to the invention at 200 ppm inhibit fungal infestation in this test to at least 80 %, while under the same conditions untreated control plants are infected by the phytopathogenic fungi to over 80 %.

Mycosphaerella graminicola (Septoria tritici) /wheat / preventive (Action against Septoria leaf spot on wheat)

[0090] 2 weeks old wheat plants cv. Riband are treated with the formulated test compound in a spray chamber. One day after application wheat plants are inoculated by spraying a spore suspension (10^6 conidia/ml) on the test plants. After an incubation period of 1 day at 22 °C /21 °C and 95% r. h. plants are kept at 22 °C / 21 °C and 70% r.h. in a greenhouse. The disease incidence is assessed 16 - 18 days after inoculation.

[0091] Compounds I.a.02, I.a.14 and I.a.20 according to the invention at 200 ppm inhibits fungal infestation in this test to at least 80 %, while under the same conditions untreated control plants are infected by the phytopathogenic fungi to over 80 %.

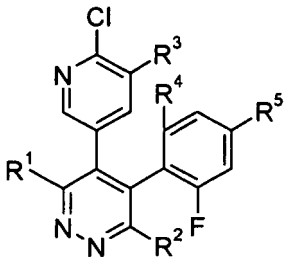
Uncinula necator (*Erysiphe necator)* / grape / preventive (Action against powdery mildew on grape)

[0092] 5 weeks old grape seedlings cv. Gutedel are treated with the formulated test compound in a spray chamber. One day after application grape plants are inoculated by shaking plants infected with grape powdery mildew above the test plants. After an incubation period of 7 days at 24 °C / 22 °C. and 70% r. h. under a light regime of 14/10 h (light/ dark) the disease incidence is assessed.

[0093] Compounds I.a.02, I.a.12, I.a.14 and I.g.11 according to the invention at 200 ppm inhibit fungal infestation in this test to at least 80 %, while under the same conditions untreated control plants are infected by the phytopathogenic fungi to over 80 %.

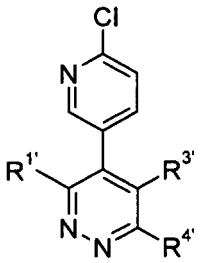
Claims

1. A compound of formula I:

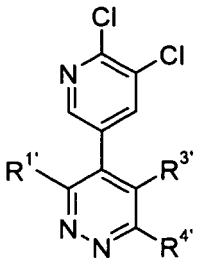


(I)

wherein
R^1 is methyl, ethyl or isopropyl;
R^2 is chloro, fluoro, hydroxy or C_1-C_2alkoxy;
R^3 is H, chloro, fluoro, methoxy or C_1-C_3alkyl;
R^4 is chloro, fluoro or bromo; and
R^5 is H, fluoro or methoxy;
or an agrochemically usable salt form thereof;
with the proviso that when R^1 is methyl, R^2 is chloro and R^3 is H, then R^4 or R^5 is different from fluoro and the compound of formula I is not (I.ae) or (I.ai) .



(I.ae)



(I.ai)

wherein $R^{1'}$, $R^{3'}$ and $R^{4'}$ are as defined as follows

$R^{1'}$	$R^{3'}$	$R^{4'}$
CH_3	2,6-difluorophenyl	Cl
CH_3	2-chloro-6-fluorophenyl	Cl
CH_3	2,6-difluoro-4-methoxyphenyl	OH
CH_3	2,6-difluoro-4-methoxyphenyl	F
CH_3	2,6-difluoro-4-methoxyphenyl	Cl
CH_3	2,6-difluoro-4-methoxyphenyl	OCH_3
CH_2CH_3	2,4-difluorophenyl	OH
CH_2CH_3	2,4-difluorophenyl	Cl
CH_2CH_3	2,4,6-trifluorophenyl	OH
CH_2CH_3	2,4,6-trifluorophenyl	Cl
CH_2CH_3	2,6-difluoro-4-methoxyphenyl	OH
CH_2CH_3	2,6-difluoro-4-methoxyphenyl	Cl

is excluded from the scope of protection.

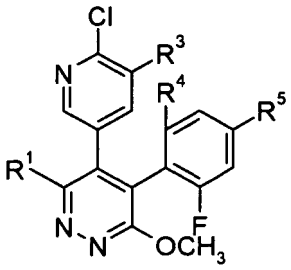
2. The compound according to claim 1 wherein
R^1 is methyl or ethyl;
R^2 is chloro, fluoro or methoxy;
R^3 is H, chloro or fluoro;
R^4 is chloro or fluoro; and
R^5 is H or methoxy.

3. The compound according to claim 1 selected from
4-(6-chloro-pyridin-3-yl)-6-methoxy-3-methyl-5-(2,4,6-trifluoro-phenyl)-pyridazine;
3-chloro-5-(6-chloro-pyridin-3-yl)-6-ethyl-4-(2,4,6-trifluoro-phenyl)-pyridazine;

3-chloro-5-(5,6-dichloro-pyridin-3-yl)-6-methyl-4-(2,4,6-trifluoro-phenyl)-pyridazine;
3-chloro-5-(6-chloro-pyridin-3-yl)-6-isopropyl-4-(2,4,6-trifluoro-phenyl)-pyridazine; and

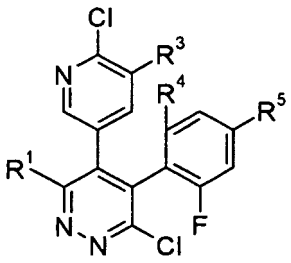
4. The compound according to claim 1 selected from
4-(6-chloro-pyridin-3-yl)-6-methoxy-3-methyl-5-(2,4,6-trifluoro-phenyl)-pyridazine;
3-chloro-5-(5,6-dichloro-pyridin-3-yl)-6-methyl-4-(2,4,6-trifluoro-phenyl)-pyridazine.

5. A process for the preparation of a compound of formula 1.2,



(I.2)

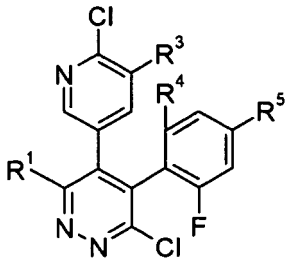
wherein R^1, R^3, R^4 and R^5 are as defined for compound of formula I, which comprises reacting a compound of formula I.1,



(I.1)

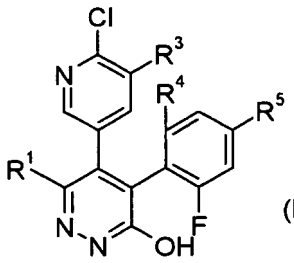
wherein R^1, R^3, R^4 and R^5 are as defined for compound of formula I, with methanol and base or with sodium methoxide.

6. A process for the preparation of a compound of formula I.1,



(I.1)

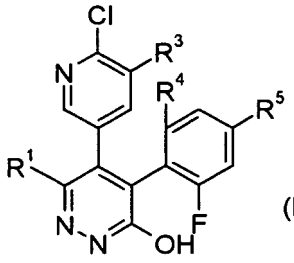
wherein R^1, R^3, R^4 and R^5 are as defined for compound of formula I, which comprises reacting a compound of formula 1.3,



(I.3)

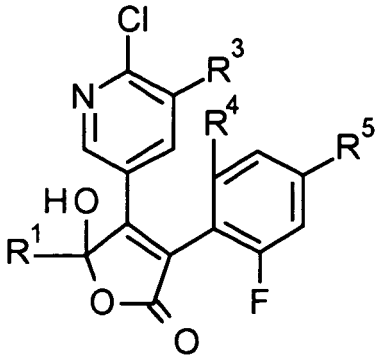
wherein R^1, R^3, R^4 and R^5 are as defined for compound of formula I, with phosphorous oxychloride or thionyl chloride.

7. A process for the preparation of a compound of formula 1.3,



(I.3)

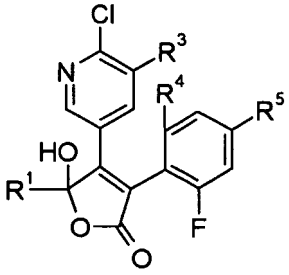
wherein R^1, R^3, R^4 and R^5 are as defined for compound of formula I, which comprises reacting a compound of formula II,



(II)

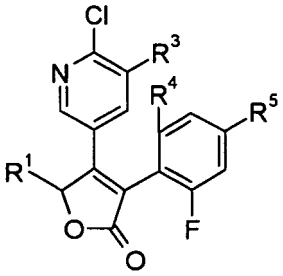
wherein R^1, R^3, R^4 and R^5 are as defined for compound of formula I, with a hydrazine derivative.

8. A process for the preparation of a compound of formula II,



(II)

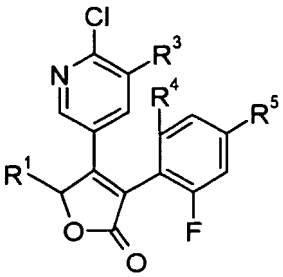
wherein R^1, R^3, R^4 and R^5 are as defined for compound of formula I, which comprises reacting a compound of formula III,



(III)

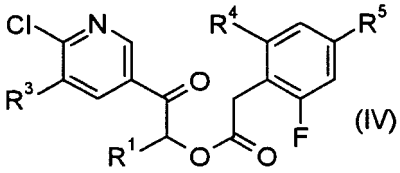
wherein R^1, R^3, R^4 and R^5 are as defined for compound of formula I, with oxygen, air, or 3-chloroperbenzoic acid.

9. A process for the preparation of a compound of formula III,



(III)

wherein R^1, R^3, R^4 and R^5 are as defined for compound of formula I, which comprises reacting a compound of formula IV,



(IV)

wherein R^1, R^3, R^4 and R^5 are as defined for compound of formula I, with a base.

10. A fungicidal composition for controlling or protecting against phytopathogenic microorganisms, comprising as active ingredient at least one compound as defined in any one of claims 1 to 4, in free form or in agrochemically usable salt form, and at least one adjuvant.

11. The composition according to claim 10 which comprises at least one additional fungicidally active compound, preferably selected from the group consisting of azoles, pyrimidinyl carbinoles, 2-amino-pyrimidines, morpholines, anilinopyrimidines, pyrroles, phenylamides, benzimidazoles, dicarboximides, carboxamides, strobilurines, dithiocarbamates, N-halomethylthiotetrahydrophthalimides, copper-compounds, nitrophenols, organo-phosphorus-derivatives, pyridazines, triazolopyrimidines, carboxamides or benzamides.

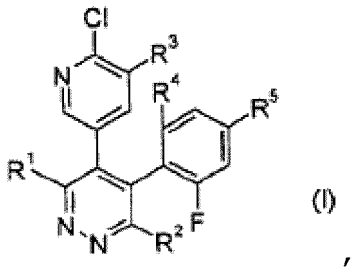
12. Use of a compound as defined in any one of claims 1 to 4 for controlling or preventing infestation of plants, harvested food crops, seeds or non-living materials by phytopathogenic microorganisms.

13. A method of controlling or preventing an infestation of crop plants, harvested food crops or non-living materials by phytopathogenic or spoilage microorganisms or organisms potentially harmful to man, which comprises the application of a compound as defined in any one of claims 1 to 4, as active ingredient to the plant, to parts of the plants or to the locus thereof, to seeds or to any part of the non-living materials, wherein the locus in not an animal.

14. The method according to claim 13, wherein the phytopathogenic microorganisms are fungal organisms.

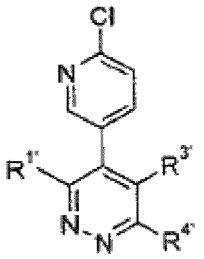
Patentansprüche

1. Verbindung der Formel I

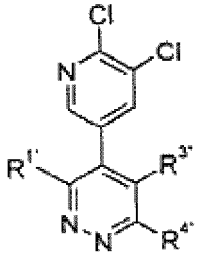


(I),

in der
R^1 Methyl, Ethyl oder Isopropyl bedeutet;
R^2 Chlor, Fluor, Hydroxy oder C_1-C_2-Alkoxy bedeutet;
R^3 H, Chlor, Fluor, Methoxy oder C_1-C_3-Alkyl bedeutet;
R^4 Chlor, Fluor oder Brom bedeutet; und
R^5 H, Fluor oder Methoxy bedeutet;
oder agrarchemisch nutzbare Salzform davon;
mit der Maßgabe, dass, wenn R^1 Methyl, R^2 Chlor und R^3 H bedeuten, dann R^4 oder R^5 nicht Fluor bedeuten und die Verbindung der Formel I nicht (I.ae) oder (I.ai) ist,



(I.ae)



(I.aī)

wobei $R^{1'}$, $R^{3'}$ und $R^{4'}$ folgendermaßen definiert sind:

$R^{1'}$	$R^{3'}$	$R^{4'}$
CH_3	2,6-Difluorphenyl	Cl
CH_3	2-Chlor-6-fluorphenyl	Cl
CH_3	2,6-Difluor-4-methoxyphenyl	OH
CH_3	2,6-Difluor-4-methoxyphenyl	F
CH_3	2,6-Difluor-4-methoxyphenyl	Cl
CH_3	2,6-Difluor-4-methoxyphenyl	OCH_3
CH_2CH_3	2,4-Difluorphenyl	OH
CH_2CH_3	2,4-Difluorphenyl	Cl
CH_2CH_3	2,4,6-Trifluorphenyl	OH
CH_2CH_3	2,4,6-Trifluorphenyl	Cl
CH_2CH_3	2,6-Difluor-4-methoxyphenyl	OH
CH_2CH_3	2,6-Difluor-4-methoxyphenyl	Cl

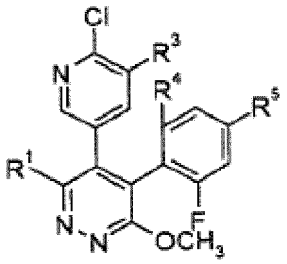
vom Schutzumfang ausgenommen ist.

2. Verbindung nach Anspruch 1, in der
R^1 Methyl oder Ethyl bedeutet;
R^2 Chlor, Fluor oder Methoxy bedeutet;
R^3 H, Chlor oder Fluor bedeutet;
R^4 Chlor oder Fluor bedeutet; und
R^5 H oder Methoxy bedeutet.

3. Verbindung nach Anspruch 1, ausgewählt aus der Reihe 4-(6-Chlorpyridin-3-yl)-6-methoxy-3-methyl-5-(2,4,6-trifluorphenyl)pyridazin; 3-Chlor-5-(6-chlorpyridin-3-yl)-6-ethyl-4-(2,4,6-trifluorphenyl)pyridazin; 3-Chlor-5-(5,6-dichlorpyridin-3-yl)-6-methyl-4-(2,4,6-trifluorphenyl)pyridazin; und 3-Chlor-5-(6-chlorpyridin-3-yl)-6-isopropyl-4-(2,4,6-trifluorphenyl)pyridazin.

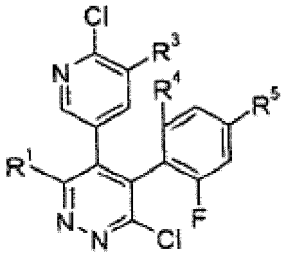
4. Verbindung nach Anspruch 1, ausgewählt aus der Reihe 4-(6-Chlorpyridin-3-yl)-6-methoxy-3-methyl-5-(2,4,6-trifluorphenyl)pyridazin; und 3-Chlor-5-(5,6-dichlorpyridin-3-yl)-6-methyl-4-(2,4,6-trifluorphenyl)pyridazin.

5. Verfahren zur Herstellung einer Verbindung der Formel 1.2,



(I.2)

in der R^1, R^3, R^4 und R^5 wie für die Verbindung der Formel I definiert sind, bei dem man eine Verbindung der Formel I.1,

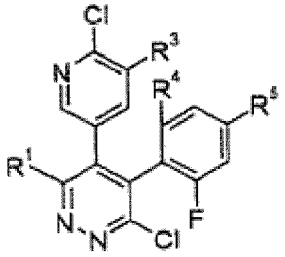


(I.1)

,

in der R^1, R^3, R^4 und R^5 wie für die Verbindung der Formel I definiert sind, mit Methanol und einer Base oder mit Natriummethanolat umsetzt.

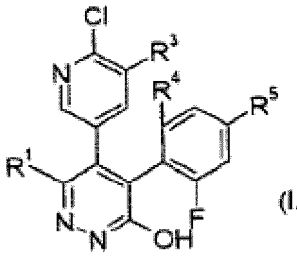
6. Verfahren zur Herstellung einer Verbindung der Formel I.1,



(I.1)

,

in der R^1, R^3, R^4 und R^5 wie für die Verbindung der Formel 1 definiert sind, bei dem man eine Verbindung der Formel 1.3,

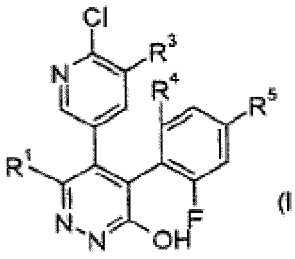


(I.3)

,

in der R^1, R^3, R^4 und R^5 wie für die Verbindung der Formel I definiert sind, mit Phosphoroxychlorid oder Thionylchlorid umsetzt.

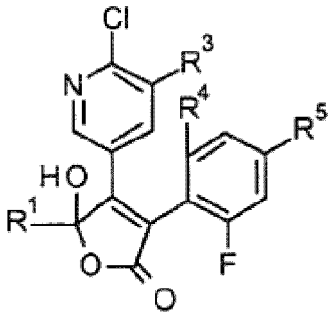
7. Verfahren zur Herstellung einer Verbindung der Formel 1.3,



(I.3)

,

in der R^1, R^3, R^4 und R^5 wie für die Verbindung der Formel I definiert sind, bei dem man eine Verbindung der Formel II,

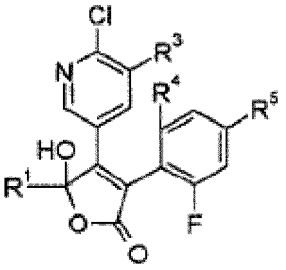


(II)

,

in der R^1, R^3, R^4 und R^5 wie für eine Verbindung der Formel I definiert sind, mit einem Hydrazinderivat umsetzt.

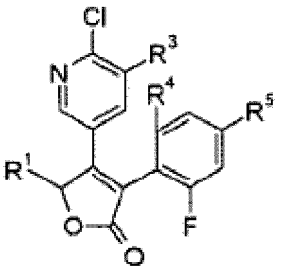
8. Verfahren zur Herstellung einer Verbindung der Formel II,



(II)

,

in der R^1, R^3, R^4 und R^5 wie für die Verbindung der Formel I definiert sind, bei dem man eine Verbindung der Formel III,

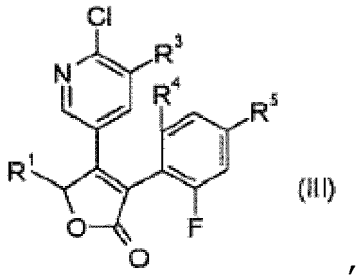


(III)

,

in der R^1, R^3, R^4 und R^5 wie für eine Verbindung der Formel I definiert sind, mit Sauerstoff, Luft oder 3-Chlorperbenzoesäure umsetzt.

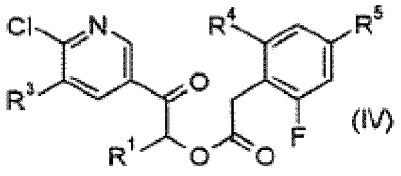
9. Verfahren zur Herstellung einer Verbindung der Formel III,



(III)

,

in der R^1, R^3, R^4 und R^5 wie für die Verbindung der Formel I definiert sind, bei dem man eine Verbindung der Formel IV,



(IV)

,

in der R^1, R^3, R^4 und R^5 wie für eine Verbindung der Formel I definiert sind, mit einer Base umsetzt.

10. Fungizide Zusammensetzung zum Bekämpfen von oder Schützen gegen phytopathogene(n) Mikroorganismen, die als Wirkstoff mindestens eine Verbindung wie in einem der Ansprüche 1 bis 4 definiert in freier Form oder in agrarchemikalisch nutzbarer Salzform sowie mindestens ein Hilfsmittel umfasst.

11. Zusammensetzung nach Anspruch 10, die mindestens eine zusätzliche fungizidwirksame Verbindung, vorzugsweise ausgewählt aus der Gruppe bestehend aus den Azolen, Pyrimidinylcarbinolen, 2-Aminopyrimidinen, Morpholinen, Anilinopyrimidinen, Pyrrolen, Phenylamiden, Benzimidazolen, Dicarboximiden, Carboxamiden, Strobilurinen, Dithiocarbamaten, N-Halogenmethylthiotetrahydrophthalimiden, Kupferverbindungen, Nitrophenolen, organischen Phosphorderivaten, Pyridazinen, Triazolopyrimidinen, Carboxamiden oder Benzamiden, umfasst.

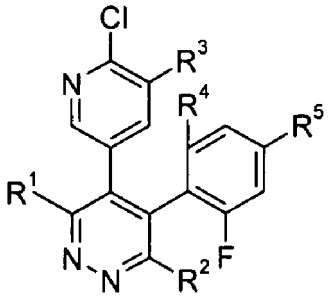
12. Verwendung einer Verbindung wie in einem der Ansprüche 1 bis 4 definiert zum Bekämpfen oder Vorbeugen von Befall von Pflanzen, geernteten Nahrungsmittelkulturen, Samen oder nichtlebenden Materialien durch phytopathogene Mikroorganismen.

13. Verfahren zum Bekämpfen oder Vorbeugen von Befall von Nutzpflanzen, geernteten Nahrungsmittelkulturen oder nichtlebenden Materialien durch phytopathogene Mikroorganismen oder Verderb verursachende Mikroorganismen oder Organismen, die möglicherweise eine Gefahr für den Menschen darstellen, bei dem man eine Verbindung wie in einem der Ansprüche 1 bis 4 definiert als Wirkstoff auf die Pflanze, auf Teile der Pflanze oder auf den Ort ihres Befindens, auf Samen oder auf einen beliebigen Teil der nichtlebenden Materialien ausbringt, wobei es sich bei dem Ort des Befindens nicht um ein Tier handelt.

14. Verfahren nach Anspruch 13, wobei es sich bei den phytopathogenen Mikroorganismen um pilzliche Organismen handelt.

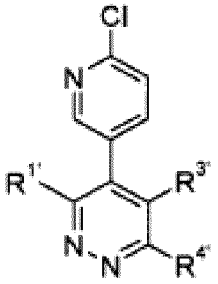
Revendications

1. Composé de formule I :

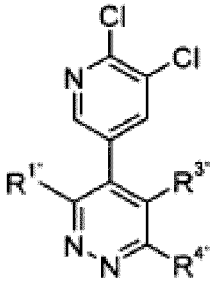


(I)

dans laquelle
R^1 est méthyle, éthyle ou isopropyle ;
R^2 est chloro, fluoro, hydroxy ou C_1-C_2alcoxy ;
R^3 est H, chloro, fluoro, méthoxy ou C_1-C_3alkyle ;
R^4 est chloro, fluoro ou bromo ; et
R^5 est H, fluoro ou méthoxy ;
ou une forme de sel utilisable sur le plan agrochimique de celui-ci ;
à condition que lorsque R^1 est méthyle, R^2 est chloro et R^3 est H, alors R^4 ou R^5 soit différent de fluoro, et le composé de formule I ne soit pas (I.ae) ou (I.ai)



(I.ae)



(I.ai)

dans lesquelles $R^{1'}$, $R^{3'}$ et $R^{4'}$ sont tels que définis ci-après :

$R^{1'}$	$R^{3'}$	$R^{4'}$
CH_3	2,6-difluorophényle	Cl
CH_3	2-chloro-6-fluorophényle	Cl
CH_3	2,6-difluoro-4-méthoxyphényle	OH
CH_3	2,6-difluoro-4-méthoxyphényle	F
CH_3	2,6-difluoro-4-méthoxyphényle	Cl
CH_3	2,6-difluoro-4-méthoxyphényle	OCH_3
CH_2CH_3	2,4-difluorophényle	OH
CH_2CH_3	2,4-difluorophényle	Cl
CH_2CH_3	2,4,6-trifluorophényle	OH
CH_2CH_3	2,4,6-trifluorophényle	Cl
CH_2CH_3	2,6-difluoro-4-méthoxyphényle	OH
CH_2CH_3	2,6-difluoro-4-méthoxyphényle	Cl

est exclu de la portée de la protection.

2. Composé selon la revendication 1, dans lequel

R^1 est méthyle ou éthyle ;
R^2 est chloro, fluoro ou méthoxy ;
R^3 est H, chloro ou fluoro ;
R^4 est chloro ou fluoro ; et
R^5 est H ou méthoxy.

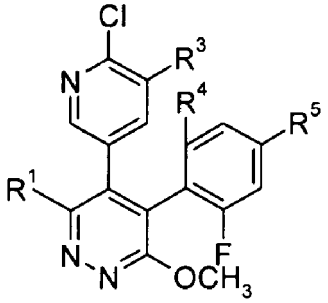
3. Composé selon la revendication 1, choisi parmi :

la 4-(6-chloropyridin-3-yl)-6-méthoxy-3-méthyl-5-(2,4,6-trifluorophényl)pyridazine ;
la 3-chloro-5-(6-chloropyridin-3-yl)-6-éthyl-4-(2,4,6-trifluorophényl)pyridazine ;
la 3-chloro-5-(5,6-dichloropyridin-3-yl)-6-méthyl-4-(2,4,6-trifluorophényl)pyridazine ; et
la 3-chloro-5-(6-chloropyridin-3-yl)-6-isopropyl-4-(2,4,6-trifluorophényl)pyridazine.

4. Composé selon la revendication 1, choisi parmi :

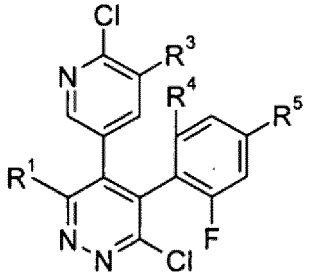
la 4-(6-chloropyridin-3-yl)-6-méthoxy-3-méthyl-5-(2,4,6-trifluorophényl)pyridazine ; et
la 3-chloro-5-(5,6-dichloropyridin-3-yl)-6-méthyl-4-(2,4,6-trifluorophényl)pyridazine.

5. Procédé de préparation d'un composé de formule I.2,



(I.2)

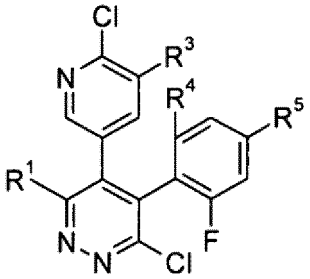
dans laquelle R^1, R^3, R^4 et R^5 sont tels que définis pour le composé de formule I, comprenant la réaction d'un composé de formule I.1,



(I.1)

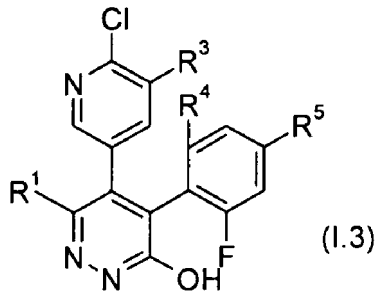
dans laquelle R^1, R^3, R^4 et R^5 sont tels que définis pour le composé de formule I, avec du méthanol et une base ou avec du méthylate de sodium.

6. Procédé de préparation d'un composé de formule I.1,



(I.1)

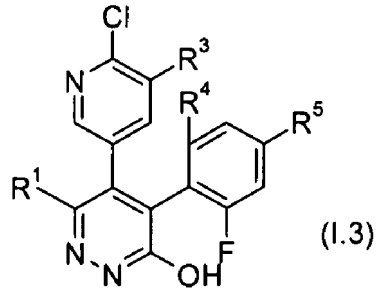
dans laquelle R^1, R^3, R^4 et R^5 sont tels que définis pour le composé de formule I, comprenant la réaction d'un composé de formule I.3,



(I.3)

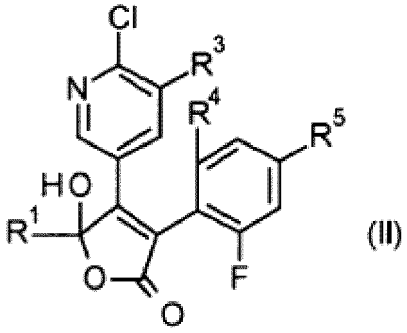
dans laquelle R^1, R^3, R^4 et R^5 sont tels que définis pour le composé de formule I, avec de l'oxychlorure de phosphore ou du chlorure de thionyle.

7. Procédé de préparation d'un composé de formule I.3,



(I.3)

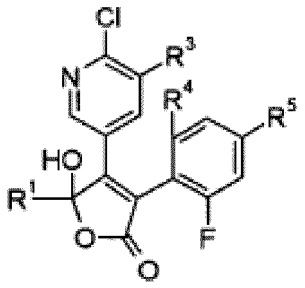
dans laquelle R^1, R^3, R^4 et R^5 sont tels que définis pour le composé de formule I, comprenant la réaction d'un composé de formule II,



(II)

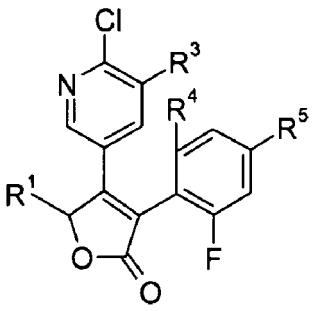
dans laquelle R^1, R^3, R^4 et R^5 sont tels que définis pour le composé de formule I, avec un dérive d'hydrazine.

8. Procédé de préparation d'un composé de formule II,



(II)

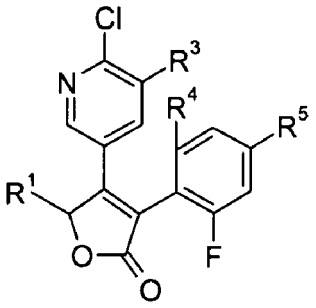
dans laquelle R^1, R^3, R^4 et R^5 sont tels que définis pour le composé de formule I, comprenant la réaction d'un composé de formule III,



(III)

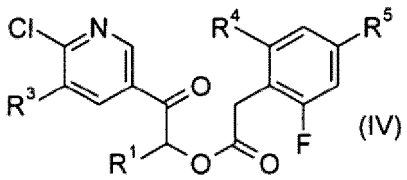
dans laquelle R^1, R^3, R^4 et R^5 sont tels que définis pour le composé de formule I, avec de l'oxygène, de l'air, ou de l'acide 3-chloroperbenzoïque.

9. Procédé de préparation d'un composé de formule III,



(III)

dans laquelle R^1, R^3, R^4 et R^5 sont tels que définis pour le composé de formule I, comprenant la réaction d'un composé de formule IV,



(IV)

dans laquelle R^1, R^3, R^3, R^4 et R^5 sont tels que définis pour le composé de formule I, avec une base.

10. Composition fongicide pour un contrôle ou une protection contre des microorganismes phytopathogènes, comprenant comme ingrédient actif au moins un composé tel que défini selon l'une quelconque des revendications 1 à 4, sous forme libre ou sous forme utilisable sur le plan agrochimique, et au moins un adjuvant.

11. Composition selon la revendication 10, comprenant au moins un autre composé actif sur le plan fongicide, choisi

de préférence dans le groupe constitué par les azoles, les pyrimidinyl-carbinoles, les 2-amino-pyrimidines, les morpholines, les anilinopyrimidines, les pyrroles, les phénylamides, les benzimidazoles, les dicarboximides, les carboxamides, les strobilurines, les dithiocarbamates, les N-halogénométhylthio-tétrahydrophtalimides, les composés à base de cuivre, les nitrophénols, les dérivés organophosphorés, les pyridazines, les triazolopyrimidines, les carboxamides ou les benzamides.

12. Utilisation d'un composé tel que défini selon l'une quelconque des revendications 1 à 4, pour un contrôle ou une prévention contre une infestation de plantes, de récoltes de cultures alimentaires, de semences ou de matériaux non vivants, par des microorganismes phytopathogènes.

13. Méthode de contrôle ou de prévention contre une infestation de plantes de culture, de récoltes de cultures alimentaires ou de matériaux non vivants, par des microorganismes phytopathogènes ou de contamination ou des microorganismes potentiellement nuisibles pour l'homme, comprenant l'application d'un composé tel que défini selon l'une quelconque des revendications 1 à 4, comme ingrédient actif, à la plante, aux parties de la plante ou au lieu où celle-ci se développe, aux semences ou à une partie quelconque des matériaux non vivants, où le lieu n'est pas un animal.

14. Méthode selon la revendication 13, dans laquelle les microorganismes phytopathogènes sont des organismes fongiques.

REFERENCES CITED IN THE DESCRIPTION

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